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(54) Color liquid cleaning and bleaching composition

(57) A colored liquid cleaning and bleaching composition is disclosed, which comprises (a) an alkali metal hypochlorite, (b) an alkali, (c) a water-soluble polymer having a sulfo group, and (d) a phthalocyanine pigment. The colored liquid cleaning and bleaching composition has stable cleaning and bleaching power and does not fade even stored for long periods.

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COLORED LIQUID CLEANING AND BLEACHING COMPOSITION

FIELD OF THE INVENTION

This invention relates to a colored liquid cleaning and bleaching composition excellent in storage stability.

BACKGROUND OF THE INVENTION

A number of cleaning compositions comprising an alkali metal hypochlorite as a base are known. Cleaning compositions of this type are now widely used for disinfection of the dishes in public facilities, cafeterias, and restaurants; bleaching of kitchen utensils and clothes; cleaning, bleaching, sweeping, disinfection or deodorizing of toilets and piping; and removal of mold gathered in bathrooms, etc.

An alkali hypochlorite is an intense oxidizing agent and needs sufficient care in handling. Taking users' safety into consideration, it has been studied to color cleaning compositions containing an alkali hypochlorite to distinguish the site where the cleaning composition has been applied. Because a colorant easily fades with time in a chlorine type oxidative bleaching agent, the choice of a colorant is of particular importance. For instance, JP-A-53-8604 discloses a method of stably coloring a hypochlorite in blue, in which a specific copper phthalocyanine pigment is added to a system comprising a hypochlorite and a caustic alkali.

However, the above-mentioned coloring method was proved to not always assure long-term storage stability of a composition with its caustic alkali concentration being reduced for higher safety, especially when stored under severe conditions. This problem cannot be solved even by combining the above-described various manipulations for improving stability of a hypochlorite. Besides, if the degree of halogen substitution on the phthalocyanine pigment exceeds a specific range, color fading will proceed during high temperature storage or long-term storage. It has thus been demanded to develop a means for further improving storage stability of a colored cleaning and bleaching composition under severe conditions or for preventing discoloration of the composition with time.

SUMMARY OF THE INVENTION

The inventors have extensively studied for obtaining a colored cleaning and bleaching composition containing an oxidative bleaching agent which is stable even when stored for a long time under severe conditions. They have found, as a result, that the object is accomplished by adding a sulfo group-containing water-soluble polymer to an alkali hypochlorite aqueous solution. To their surprise, it has been confirmed that application of the above stabilizing method to a system colored with a phthalocyanine pigment makes it possible to provide a colored cleaning and bleaching composition which stably retains a blue to green color

without specifically limiting the degree of halogen substitution of the phthalocyanine pigment.

Namely, the present invention provides a colored liquid cleaning and bleaching composition comprising the following components (a) to (d):

(a) an alkali metal hypochlorite;

(b) an alkali;

(c) a water-soluble polymer having a sulfo group; and

(d) a phthalocyanine pigment.

DETAILED DESCRIPTION OF THE INVENTION

The colored liquid cleaning and bleaching composition of the present invention, will be described below in detail.

The alkali metal hypochlorite (a) is preferably used in an amount of from 0.1 to 10 % by weight, and more preferably from 1 to 6 % by weight, based on the total weight of the composition. If the amount of component (a) is less than 0.1 %, the composition has insufficient bleaching performance, particularly bleaching speed. If it exceeds 10 %, the composition is instable and tends to undergo phase separation or give off an offensive smell and is not suitable as a commercial product. Preferred examples of the alkali metal hypochlorite as component (a) include potassium hypochlorite, sodium hypochlorite, and a mixture thereof at an arbitrary mixing ratio. An alkali metal hypochlorite generally contains sodium chloride. Reduction of the sodium chloride content to 5 % by weight or less is effective to

improve stability of the composition. Other alkali metal salts of hypohalogenous acid are unsuitable from the aspects of cost and safety.

The alkali as component (b) is not particularly limited and includes a caustic alkali such as sodium hydroxide, and a silicate such as sodium metasilicate, either alone or as a mixture thereof at an arbitrary mixing ratio. The alkali (b) is preferably used in a total amount of from 0.1 to 5 % by weight, and more preferably from 0.5 to 3 % by weight, based on the total weight of the composition. If the amount of component (b) is less than 0.1 %, the stability of the composition is deteriorated. If it exceeds 5 %, irritation to the skin or eyes increases.

The sulfo-containing water-soluble polymer as component (c), which serves as a dispersant, includes a water-soluble polymer comprising a formaldehyde condensate of an aromatic compound containing a sulfo group or a sulfonate group and a salt thereof, and a homo- or copolymer comprising one or more monomers selected from styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, allylsulfonic acid, vinylsulfonic acid, metallylsulfonic acid, sulfopropyl methacrylate, and a salt of these monomers. The sulfo- or sulfonate-containing aromatic compound is preferably selected from petroleum sulfonic acid or a salt thereof, naphthalene-sulfonic acid or a salt thereof, lignin sulfonic acid or a salt thereof, creosote oil sulfonic acid or a salt thereof,

and a cresol alkylenesulfonic acid or a salt thereof. Specific examples of the sulfo-containing water-soluble polymer (c) include a salt of a condensate of metacresol-methylenesulfonic acid-Schaffer's acid and formalin (e.g., "Demol SSL", tradename, a product produced by Kao Corporation), a salt of a condensate of metacresolmethylenesulfonic acid and formalin (e.g., "Demol SC30", tradename, a product produced by Kao Corporation), a salt of a condensate of creosote oil sulfonic acid and formalin (e.g., "Demol C", tradename, a product produced by Kao Corporation), a salt of a condensate of a naphthalenesulfonate and formalin (e.g., "Demol NL", tradename, a product produced by Kao Corporation), a salt of a condensate of lignin sulfonate and formalin, a salt of a condensate of melaminesulfonic acid and formalin, a sodium styrenesulfonate polymer salt, and a salt of sulfonated product of polystyrene. The water-soluble polymer to be used in the present invention preferably has a molecular weight of from 1,000 to 2,000,000, or a polymerization degree of from 2 to 20. Preferred examples of the salt of the water-soluble polymer include alkali metal salts such as sodium salt and potassium salt.

Among them, a naphthalenesulfonate-formalin condensate salt, a metacresolmethylenesulfonic acid-Schaffer's acid-formalin condensate salt, a metacresol-methylenesulfonic acid-formalin condensate salt, and a creosote oil sulfonic acid-formalin condensate salt are

preferred and a naphthalenesulfonate-formalin condensate salt is particular preferred from their stabilizing effect on a phthalocyanine pigment in the composition during storage.

Component (c) is preferably used in an amount of from 0.001 to 1 % by weight, and more preferably from 0.01 to 0.5 % by weight, based on the total weight of the composition.

The phthalocyanine pigment as component (d) is represented by formula (I):

$$C_{32}H_{(16-n)}X_nN_8M \qquad (I)$$

wherein n is 0 or an integer of from 1 to 16; X is a halogen atom; and M is a metallic atom.

X is preferably one of or a combination of two or more of Br, I, and Cl. M is preferably one of or a combination of two or more of Fe, Co, and Cu, more preferably Cu. It was confirmed that a sulfonate or carboxylate of the compound represented by the above formula produces no effect of improving stability of the composition.

Any of the phthalocyanine compounds represented by the above formula wherein the number of halogen substituents is from 0 to 16 is effective either alone or in the form of a mixed pigment for adjusting the color.

The phthalocyanine pigment (d) is preferably used in an amount of from 0.00001 to 0.01 % by weight based on the total weight of the composition. If the amount of component (d) is less than 0.00001%, the coloring effect is

insubstantial. If it exceeds 0.01 %, the dispersion stability of the composition is reduced.

Component (d) is available in the form of an aqueous dispersion at room temperature usually having a dispersed particle size of from 0.01 to 0.3 μm.

It is preferable that a weight ratio of components (c) to (d) in the composition falls within a range of from 10 to 1000.

If desired, the colored liquid cleaning and bleaching composition of the present invention may contain surfactants conventionally employed in the art. Preferred examples of the surfactant include (i) a tertiary amine oxide represented by formula (II):

$$R_1R_2R_3N\rightarrow O \qquad \text{(II)}$$

wherein R_1 represents a straight chain or branched alkyl group having from 8 to 20 carbon atoms; and R_2 and R_3 each represent a straight chain or branched alkyl group having from 1 to 3 carbon atoms; (ii) an alkali metal salt of a saturated fatty acid having from 8 to 18 carbon atoms; (iii) a straight chain alkylbenzenesulfonate having from 8 to 18 carbon atoms in the alkyl moiety thereof and/or a straight chain alkylnaphthalenesulfonate having from 8 to 18 carbon atoms in the alkyl moiety thereof; and a combination of the surfactants (i) to (iii). Preferably, the surfactants (i) to (iii) are each present in the composition in an amount of from 0.1 to 5

% by weight, with the (i) to (ii) weight ratio being from 50:50 to 25:75, and more preferably from 49:51 to 35:65. If the (i) to (ii) weight ratio is out of this range, the composition tends to be too viscous for obtaining convenience for use. The surfactants (i), (ii), and (iii) are preferably used in a total amount of from 0.3 to 15 % by weight based on the total weight of the composition.

In formula (II) given for tertiary amine oxide (i), the alkyl group as R_1 includes octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl groups, with dodecyl and tetradecyl groups being preferred. R_1 may be a mixed alkyl group having different carbon atom numbers derived from a naturally occurring substance. The alkyl group as R_2 or R_3 includes methyl, ethyl and propyl groups, with a methyl group being preferred. Specific examples of tertiary amine oxide (i) are lauryldimethylamine oxide, myristyldimethylamine oxide, and coco-dimethylamine oxide.

Alkali metal salt (ii) includes a sodium or potassium salt of a saturated fatty acid, e.g., lauric acid, myristic acid, palmitic acid, stearic acid, etc.

In alkylbenzenesulfonate and/or alkylnaphthalene-sulfonate (iii), the alkyl group on the benzene or naphthalene ring is a straight chain alkyl group containing from 8 to 18 carbon atoms.

The system may further be stabilized by thickening with a combination of the above-mentioned surfactants or an

electrolyte, such as an inorganic water-soluble salt (e.g., sodium chloride, Grauber's salt, a calcium salt or a magnesium salt) in a known manner. Stabilization of the system may also be effected by trapping trace amounts of heavy metals present in the system by addition of a chelating agent according to a known technique. Examples of applicable chelating agents are aminophosphonic acid N-oxides, and especially, (nitrilotris(methylene))triphosphonic acid N-oxide, 2-phosphonobutane-1,2,4-tricarboxylic acid salts, 1-hydroxyethane-1,1-diphosphonic acid salts, and crosslinked polycarboxylic acid salts. The aminophosphonic acid N-oxide chelating agent(s) may be added to the colored liquid cleaning and bleaching composition of the invention in an amount of from 0.001 to 0.3 % by weight, preferably from 0.01 to 0.2 % by weight. Some known sequestering agents, such as an aminocarboxylic acid type (e.g., an ethylene-diaminetetraacetate or a nitrilotriacetate), an oxycarboxylic acid type (e.g., a citrate, a malate or a tartrate), a dicarboxylate type (e.g., succinic acid, glutaric acid or adipic acid), and a phosphate type (e.g., a pyrophosphate, a tripolyphosphate or a hexametaphosphate) undergo considerable decomposition in a hypochlorous acid aqueous solution and are not suitable.

Further, the composition may contain builders, such as aromatic sulfonates (e.g., toluenesulfonates, xylene-sulfonates, cumenesulfonates, and naphthalenesulfonates);

fluorescent dyes; radical scavenger (e.g., BHT); abrasives (e.g., calcium carbonate, silica, montmorillonite, and smectite); and flavors such as terpene alcohols.

The colored liquid cleaning and bleaching composition of the present invention is usually prepared by mixing the above-mentioned essential components and optional components with a balancing amount of water.

The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the present invention is not construed as being limited thereto.

EXAMPLE 1

Colored liquid cleaning and bleaching composition were prepared according to the formulation shown in Table 1 below. The storage stability of each composition and the color stability after storage were evaluated as follows. The results obtained are shown in the Table.

1) Storage Stability:

Each composition measuring 600 mℓ was sealed in a polyethylene cylinder bottle ("Hiter Bottle"; full capacity: 725 mℓ; bottom wall thickness: 0.6 mm) and stored at 40°C for 3 months. The contents of the bottle were taken out, and the swell of the cylinder bottle was observed with the naked eye.

Criteria for Evaluation:

A: No change

B: The bottle became rickety due to slight swelling at the bottom.

C: The bottle fell down due to swelling at the bottom (the same state resulted when an inner pressure of 0.6 kg/cm^2 was applied).

2) Color Stability:

An aliquot of the composition having been stored in the test of storage stability was observed with the naked eye and rated "A" (no color change), "B" (slight discoloration) or "C" (discoloration).

TABLE 1

	Product of the Invention					Comparative Product		
	1	2	3	4	5	1	2	3
Composition: (% by weight)								
Sodium hypochlorite	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sodium hydroxide	1	1	0.5	1	1	1	1	1
Sodium metasilicate	-	0.5	-	-	-	-	-	-
Naphthalenesulfonic acid-formalin condensate[1)]	0.5	0.5	0.5	-	-	-	-	-
Metacresolmethylene-sulfonic acid-formalin condensate condensate[2)]	-	-	-	0.5	-	-	-	-
Sodium styrene-sulfonate polymer[3)]	-	-	-	-	0.5	-	-	-
$C_{32}H_{11}Cl_5N_8Cu$	0.005	-	-	0.005	-	0.005	-	-
$C_{32}H_2Cl_{14}N_8Cu$	-	0.005	0.005	-	0.005	-	0.005	-
$C_{32}H_{13}N_8Cu(SO_3Na)_3$	-	-	-	-	-	-	-	0.005
Ion exchanged water	balance[4)]	balance	balance	balance	balance	balance	balance	balance
Stability:								
Storage stability	A	A	A	A	A	C	B	C
Color stability	A	A	A	A	A	A	C	C

Note: 1): Demol NL, tradename, a product produced by Kao Corporation

2): Demol SC 30, tradename, a product produced by Kao Corporation

3): PolyNass PS-1, tradename, a product produced by Tosoh Corporation

4): To make 100 % by wight

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims:

1. A colored liquid cleaning and bleaching composition comprising the following components (a) to (d):

(a) an alkali metal hypochlorite;

(b) an alkali;

(c) a water-soluble polymer having a sulfo group; and

(d) a phthalocyanine pigment represented by formula (I):

$$C_{32}H_{(16-n)}X_nN_8M \qquad (I)$$

wherein n is 0 or an integer of from 1 to 16; X is a halogen atom; and M is a metallic atom.

2. The colored liquid cleaning and bleaching composition of claim 1, wherein said water-soluble polymer having a sulfo group is selected from the group consisting of a water-soluble polymer comprising a formaldehyde condensate of an aromatic compound containing a sulfo group or a sulfonate group and a salt thereof, and a homo- or copolymer comprising one or more monomers selected from styrenesulfonic acid, 2-acrylamide-2-methylpropanesulfonic acid, allylsulfonic acid, vinylsulfonic acid, metallylsulfonic acid, sulfopropyl methacrylate, and a salt of these monomers.

3. The colored liquid cleaning and bleaching composition of claim 2, wherein said aromatic compound containing a sulfo group or a sulfonate group is selected from the group consisting of petroleum sulfonic acid and a salt thereof, naphthalenesulfonic acid and a salt thereof,

lignin sulfonic acid and a salt thereof, creosote oil sulfonic acid and a salt thereof, and a cresol alkylenesulfonic acid and a salt thereof.

4. A colored liquid cleaning and bleaching composition comprising the following components (a) to (d):

(a) from 0.1 to 10 % by weight of an alkali metal hypochlorite;

(b) from 0.1 to 5 % by weight of an alkali;

(c) from 0.001 to 1 % by weight of a water-soluble polymer having a sulfo group; and

(d) from 0.00001 to 0.01 % by weight of a phthalocyanine pigment represented by formula (I):

$$C_{32}H_{(16-n)}X_nN_8M \qquad (I)$$

wherein n is 0 or an integer of 1 to 16; X is a halogen atom; and M is a metallic atom,

provided that the weight ratio of component (c) to component (d) is from 10 to 1,000.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report) 16	Application number GB 9318936.3
Relevant Technical Fields (i) UK Cl (Ed.L) C5D (DGA, DHC, DJA) (ii) Int Cl (Ed.5) C11D 3/37, 3/39, 3/40	Search Examiner C SHERRINGTON Date of completion of Search 20 DECEMBER 1993
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI, CLAIMS	Documents considered relevant following a search in respect of Claims :- 1-4

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Category	Identity of document and relevant passages	Relevant to claim(s)
A	EP 0079102 A1 (UNILEVER PLC) whole document	1-4
A	WPI Abstract Accession No 90-309129/41 and JP 020218798 A	1-4

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